

**Original citation:**

Brunt, D., Balakrishnan, Geetha, Mayoh, Daniel, Lees, Martin R., Gorbunov, D., Qureshi, N. and Petrenko, Oleg. (2018) Magnetisation process in the rare earth tetraborides, NdB<sub>4</sub> and HoB<sub>4</sub>. Scientific Reports, 8 (1). 232.

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# SCIENTIFIC REPORTS

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## Magnetisation process in the rare earth tetraborides, $\text{NdB}_4$ and $\text{HoB}_4$

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Received: 22 September 2017

Accepted: 6 December 2017

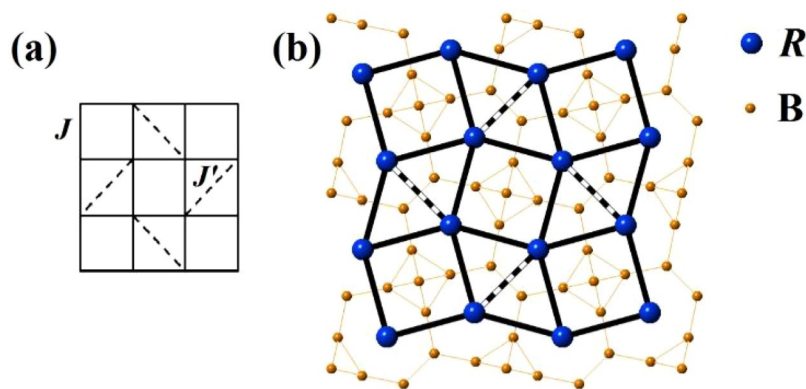
Published online: 10 January 2018

A field-induced magnetisation process in the frustrated antiferromagnets is often much richer compared to the materials without competing interactions. The applied field tends to stabilise unusual spin configurations which frequently results in the appearance of magnetisation plateaux. Here we report a study into the field-induced magnetisation of the two frustrated rare earth tetraborides,  $\text{HoB}_4$  and  $\text{NdB}_4$ .  $\text{NdB}_4$  shows a fractional magnetisation plateau occurring at  $M/M_{\text{sat}} \approx \frac{1}{5}$  before saturating in a field of 33 kOe. On cooling down to 0.5 K the temperature dependent susceptibility of  $\text{NdB}_4$  shows an unconventional transition where the system returns to the zero field antiferromagnetic state from a higher-temperature ferrimagnetic state. We are able to reconstruct the magnetic phase diagram of  $\text{NdB}_4$  from the magnetisation, susceptibility and resistivity measurements for both  $H \parallel c$  and  $H \perp c$ . For  $\text{HoB}_4$ , the most interesting behaviour is found at the lowest temperature of 0.5 K, where the field dependent magnetisation demonstrates a new fractional  $\frac{1}{2}$ -magnetisation plateau. Further insight into the relations between the exchange interactions and single ion effects is gained through high-field magnetisation measurements in both  $\text{HoB}_4$  and  $\text{NdB}_4$ .

In the presence of antiferromagnetic interactions, lattices based around edge and corner sharing-triangles<sup>1</sup> and tetrahedra<sup>2</sup> display geometric frustration. These systems are unable to minimise the energy of the competing interactions resulting in a large ground-state degeneracy<sup>3</sup>. This leads to a suppression of the long-range order and often results in a diverse magnetic phase diagrams. Some notable examples include the pyrochlore<sup>4</sup>, garnet<sup>5</sup> and kagome lattices<sup>6</sup>. In particular, materials such as  $\text{SrCu}_2(\text{BO}_3)_2$ <sup>7</sup> and the rare earth tetraboride ( $\text{RB}_4$ ) family, based on the frustrated Shastry-Sutherland lattice (SSL)<sup>8</sup> (Fig. 1(a)) have garnered attention due to their complex phase diagrams, displaying a variety of magnetic phases in quite modest magnetic fields. The  $\text{RB}_4$  family crystallises into a tetragonal ( $P4/mbm$ ) structure, where the  $R$  ions form a network of squares and triangles in the  $ab$  plane, which topologically maps to the SSL (Fig. 1(b)). The usual order amongst the  $\text{RB}_4$  is antiferromagnetic with the typical ordering being confined to the  $ab$  plane. One of the  $R^{3+}$  ion valence electrons is given up to the conduction band making the  $\text{RB}_4$  family metallic and it is believed the RKKY interaction is important in the formation of long-range order of the magnetic moment on the rare earth ions only<sup>9</sup>. Plateaux with fractional values of the saturation magnetisation,  $M_{\text{sat}}$ , are a common feature to many of the  $\text{RB}_4$  family members ranging from a  $M/M_{\text{sat}} = \frac{1}{5}$ , corresponding to a ferrimagnetic phase in  $\text{ErB}_4$ <sup>10</sup> to a more complex striped structure displayed in  $\text{TmB}_4$ <sup>11</sup>. While in some cases high magnetic fields are needed to observe the fractional plateaux<sup>12,13</sup>.

The initial study of the SSL considered three cases; the quantum, Ising and classical limit<sup>8</sup>. The classical limit in particular is well suited to describing the  $\text{RB}_4$  family due to the relatively large magnetic moment arising from the  $R^{3+}$  ions. It was found that in this limit the SSL has an exact ground-state solution, with a helical arrangement of the magnetic moments. Significant theoretical work has been done more recently using Heisenberg<sup>14,15</sup> and Ising<sup>16–18</sup> spins in the classical limit to understand the  $\text{RB}_4$  family. Many of these studies predict the existence of fractional magnetisation plateaux. For  $\text{HoB}_4$  in particular it was suggested the  $\frac{1}{3}$  plateau could be due to an *up-up-down* collinear arrangement on the Ho moments in the triangle formed by the diagonal  $J'$ , while another suggestion is an “umbrella” structure where the moments are tilted towards the vertical axis and are arranged at  $120^\circ$  relative to one another forming a spiral that propagates through the structure<sup>14,18</sup>. The introduction of further interactions beyond  $J$  and  $J'$ , including the RKKY interaction<sup>19</sup>, dipolar interaction<sup>16</sup> and longer range interactions across multiple unit cells<sup>15</sup>, have predicted the emergence of further smaller features in the magnetisation

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**Figure 1.** (a) Shastry-Sutherland lattice, (b) projection of  $RB_4$  structure along the tetragonal  $c$  axis. The  $R$  ions form a lattice that topologically maps to the Shastry-Sutherland lattice. Solid bonds correspond to the nearest neighbour interaction  $J$ , while the dashed bonds are the next nearest neighbour  $J'$ .

curves. Thus gaining an insight into the exchange interactions  $J$  and  $J'$  is an important first step to understanding the  $RB_4$  family.

In this report we have investigated the magnetisation process in two members of the  $RB_4$  family,  $HoB_4$  and  $NdB_4$ . We follow the development of the magnetic order in these compounds with an applied field by measuring magnetisation and susceptibility down to  $T = 0.5$  K and observe a sequence of unconventional transitions. The magnetisation measurements are extended to high fields for both  $HoB_4$  and  $NdB_4$ . For  $NdB_4$  we also present field and temperature dependent resistivity measurements and construct the  $H - T$  magnetic phase diagrams for both  $H \parallel c$  and  $H \perp c$ .

$HoB_4$  shows successive phase transitions at  $T_{N1}^{Ho} = 7.1$  K and  $T_{N2}^{Ho} = 5.7$  K, defining the intermediate temperature ( $T_{N2}^{Ho} < T < T_{N1}^{Ho}$ ) and low temperature ( $T < T_{N2}^{Ho}$ ) magnetically ordered phases<sup>20</sup>. The magnetic structure for both phases has been determined by powder neutron diffraction<sup>21</sup>. The intermediate temperature phase has an incommensurate amplitude modulated magnetic order in which the moments are tilted from the  $c$  axis by approximately  $25^\circ$  towards the  $[110]$  direction. The order is characterised by the propagation vector  $(\delta, \delta, \delta')$ , where  $\delta = 0.022$  and  $\delta' = 0.43$ . The low temperature phase is ordered with a non-collinear antiferromagnetic state.

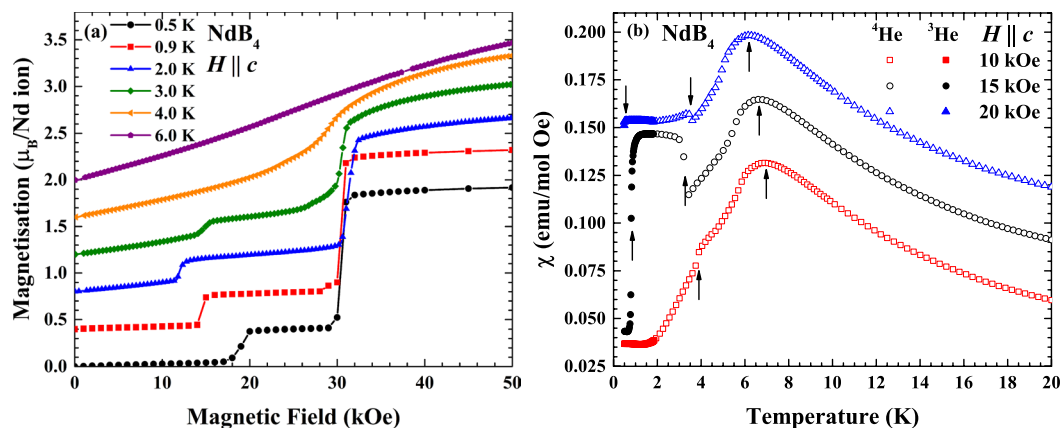
Fractional magnetisation plateaux at  $M/M_{sat} = \frac{1}{3}$ , with two less pronounced features at  $M/M_{sat} \approx \frac{4}{9}$  and  $\frac{3}{5}$  have been observed in field dependent magnetisation measurements<sup>20,22</sup>. Single crystal neutron diffraction measurements have revealed the  $\frac{1}{3}$ -magnetisation plateau has a ferrimagnetic structure where ferromagnetic layers stack in an up-up-down configuration, with the moments pointing along the  $c$  axis<sup>23</sup>.

Heat capacity and magnetic susceptibility measurements on  $NdB_4$  show successive phase transitions at  $T_0^{Nd} = 17$  K,  $T_{N1}^{Nd} = 7.0$  K and  $T_{N2}^{Nd} = 4.8$  K<sup>24</sup>. The three transitions define the high ( $T_{N1}^{Nd} < T < T_0^{Nd}$ ), intermediate ( $T_{N2}^{Nd} < T < T_{N1}^{Nd}$ ) and low ( $T < T_{N2}^{Nd}$ ) temperature ordered phases in  $NdB_4$ . These have been attributed to quadrupolar ordering, incommensurate and fully ordered phases respectively<sup>24</sup>. Although recently the commensurate magnetic structure in the high temperature phase has been determined to have an “all-in/all-out” antiferromagnetic order where the moments on four Nd ions in the unit cell are in the  $ab$  plane and point into the square formed by the Nd ions, cooling causes the the moments to rotate in the  $ab$  plane slightly. On the other hand the intermediate and low temperatures phases were found to be incommensurate<sup>25</sup>.

The structure of this report is as follows. The results and discussion is split into two subsections. The  $NdB_4$  subsection shows the magnetisation and resistivity measurements for  $NdB_4$  bringing all the measurements together in a magnetic phase diagram, while the next subsection shows the low-temperature and high-field magnetisation for  $HoB_4$ . The next section summarises the findings. Finally the experimental details are described in the methods section.

## Results and Discussion

**$NdB_4$ .** Figure 2(a) shows the field dependent magnetisation curves for  $NdB_4$  single crystal samples. The temperature was varied between 0.5 and 6 K. For all temperatures below  $T_{N2}^{Nd} = 4.8$  K the magnetisation curves indicate the presence of a plateau, which becomes more pronounced at lower temperatures. By  $T = 0.5$  K the plateau is clearly defined by the lower and higher field transitions at  $H = 20$  and 30 kOe respectively, the value of magnetisation on a plateau is approximately  $\frac{1}{5}$  of the values observed in higher fields. While the transition at 30 kOe is almost temperature independent, the temperature dependence of the critical field of the transition to the plateau from lower fields appears to be non-monotonic. On warming from 0.5 K, the value of the transition decreases to 14 and to 12 kOe for 0.9 and 2 K respectively before increasing to 15 kOe at 3 K, with the plateau becoming less defined. While the transition to saturation at 3 K begins with a gradual up turn at approximately  $H = 26$  kOe before a more significant jump at approximately 29 kOe. Increasing the temperature further to  $T = 4$  K, the magnetisation plateau becomes significantly less pronounced and the transitions could only be seen in the derivatives of the magnetisation curve,  $dM/dH$  (not shown). For  $T = 4$  K, the lower-field transition appears to be shift to 24 kOe, while the higher-field transition remains at approximately 30 kOe. The magnetisation curve at  $T = 6$  K (in the intermediate temperature phase) shows no discernible transition, linearly increasing towards saturation.



**Figure 2.** (a) Field dependent magnetisation curves of  $\text{NdB}_4$  for  $H \parallel c$ . Each curve is subsequently offset by  $0.4 \mu_B$  per Nd ion. (b) Temperature dependent magnetic susceptibility curves at 10, 15 and 20 kOe with  $H \parallel c$ . Open symbols correspond to measurements taken using  $^4\text{He}$ , while closed symbols correspond to those made using  $^3\text{He}$  and each curve is subsequently offset by  $0.03 \text{ emu/mol-Oe}$ . The arrows correspond to the position of the magnetic phase transitions.

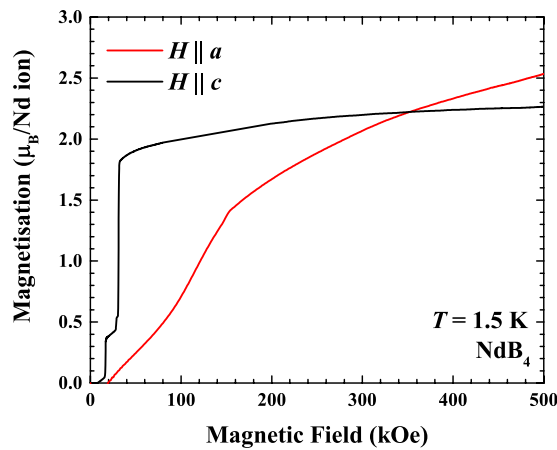
The exact nature of the plateau phase is currently unknown, however, a  $\frac{1}{5}$ -magnetisation plateau is quite unusual as there are only four magnetic moments in the unit cell. Magnetisation plateaux with fractional values of  $\frac{1}{7}$  and  $\frac{1}{9}$  have been observed in  $\text{TmB}_4$ <sup>11</sup>. Here neutron diffraction measurements revealed these phases had a striped structure consisting of antiferromagnetic regions 7 or 9 unit cells wide respectively, separated by a strip of ferromagnetic spins<sup>11</sup>. Alternatively the plateau arise from stacks of ferromagnetic layers along the  $c$  axis, similar to the proposed field-induced structure in  $\text{HoB}_4$ <sup>23</sup>. Above  $H = 30 \text{ kOe}$ , the magnetisation value is approximately  $2 \mu_B$  per Nd ion, remaining constant up to 100 kOe. The sample appears to have reached saturation, however, the saturated moment is significantly smaller compared to the expected saturated moment of  $3.2 \mu_B$  for  $\text{Nd}^{3+}$  ions.

To investigate this unusual temperature dependence of the transition field to the  $\frac{1}{5}$ -magnetisation plateau, magnetic susceptibility measurements at 10, 15 and 20 kOe were made, as shown in Fig. 2(b). The susceptibility curve at  $H = 10 \text{ kOe}$  shows a broad maximum at  $T = 6.8 \text{ K}$  and a discontinuous drop at  $T = 4.2 \text{ K}$ . These correspond to transitions to the incommensurate intermediate and low temperature phases. Increasing the field to 15 kOe the broad maximum is suppressed to  $T = 6.7 \text{ K}$ , while there is now a jump at  $T = 3.3 \text{ K}$ , which is the magnetisation plateau state. Cooling further reveals a drop in the susceptibility at  $T = 0.8 \text{ K}$ . Temperature dependent susceptibility at lower fields shows no indication of a new phase, suggesting the transition is a re-entrant phase transition occurring at  $T = 0.8 \text{ K}$  where the field induced state returns to the zero-field antiferromagnetic state. Increasing the field to 20 kOe,  $T_{\text{N1}}^{\text{Nd}}$  is further suppressed to 6.2 K, while  $T_{\text{N2}}^{\text{Nd}}$  increases to 3.6 K. It can also be seen that the lower, novel transition is suppressed with the transition beginning at  $T \approx 0.5 \text{ K}$ , but we are unable to achieve lower temperatures to clearly see the entire transition.

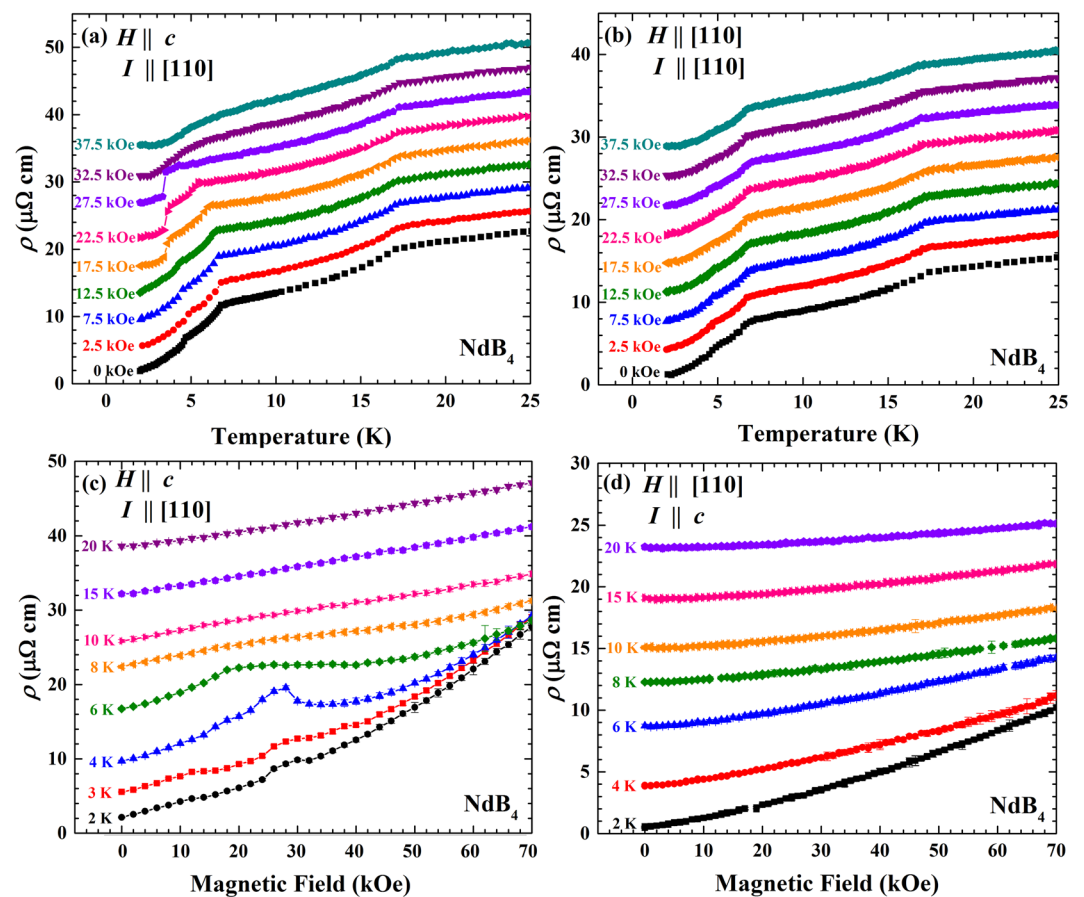
Figure 3 shows the field dependent magnetisation of  $\text{NdB}_4$  at  $T = 2 \text{ K}$  for  $H \parallel c$  and  $H \perp c$  in a pulsed magnetic field up to 500 kOe. For  $H \parallel c$ , we observe the  $\frac{1}{5}$ -magnetisation plateau at 14 kOe and then the transition to saturation at 30 kOe. The magnetisation then increases only marginally from  $2.0 \mu_B$  per Nd ion in 100 kOe up to  $2.3 \mu_B$  in 500 kOe. The difference between the saturated moment and expected moment could be arising due to strong crystalline electric field effects<sup>26</sup>. For  $H \perp c$  on the other hand, the magnetisation is linear up to approximately 70 kOe, with a gradual up turn in the value showing a distinct change in gradient at approximately 150 kOe. After the transition the magnetisation increases, surpassing the magnetisation of  $H \parallel c$  at 350 kOe, the magnetisation continues to increase towards saturation, achieving  $2.6 \mu_B$  per Nd ion by 500 kOe. The difference between the two directions suggest the easy axis in high fields is along the  $a$  axis.

The temperature dependence of the resistivity of  $\text{NdB}_4$  single crystal samples is shown in Fig. 4 for both  $H \parallel c$  and  $H \perp c$ . The  $\text{NdB}_4$  crystal studied has a high residual resistance ratio value (RRR;  $\rho(300 \text{ K})/\rho(2 \text{ K}) = 100$ ) suggesting a high quality sample. For both field directions the resistivity curves are linear in temperature down to the first transition,  $T_0^{\text{Nd}}$ , indicating the metallic nature of  $\text{NdB}_4$  which is the case in the other  $\text{RB}_4$  family members. There is a sudden drop in the resistivity at  $T_0^{\text{Nd}} = 17 \text{ K}$ , with two further features at  $T_{\text{N1}}^{\text{Nd}} = 6.8 \text{ K}$  and  $T_{\text{N2}}^{\text{Nd}} = 4.9 \text{ K}$ . The sudden slope change could be due to the loss of spin disorder scattering at the antiferromagnetic transition temperature, which has been suggested for other members of the  $\text{RB}_4$  family<sup>27,28</sup>. The evolution of the temperature dependence of the resistivity in field for  $H \parallel c$  is shown in Fig. 4(a). Similarly to previously published magnetic susceptibility curves<sup>24</sup>, the transitions at  $T_{\text{N1}}^{\text{Nd}}$  and  $T_{\text{N2}}^{\text{Nd}}$  are suppressed with increasing field.  $T_{\text{N2}}^{\text{Nd}}$  becomes significantly more pronounced for  $H = 17.5, 22.5$  and  $27.5 \text{ kOe}$ , which corresponds to the transitions into the  $\frac{1}{5}$ -magnetisation plateau phase. The transition becomes very broad above 27.5 kOe as the system tends towards a polarised state.

The temperature dependence of the resistivity for  $H \perp c$  is shown in Fig. 4(b). We observe the three transitions at  $T_0^{\text{Nd}}$ ,  $T_{\text{N1}}^{\text{Nd}}$  and  $T_{\text{N2}}^{\text{Nd}}$ , which do not change significantly between  $0 \leq H \leq 37.5 \text{ kOe}$ , mirroring the magnetic susceptibility and heat capacity measurements<sup>24</sup>.



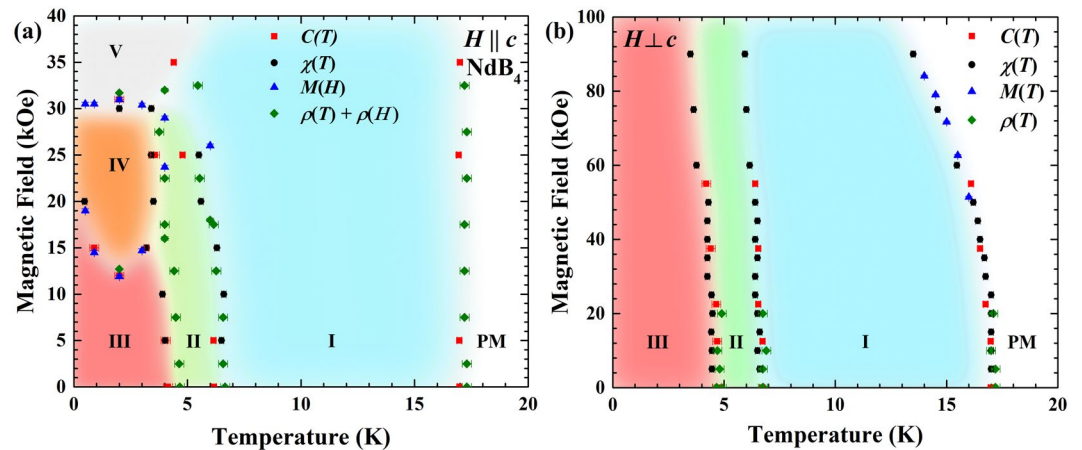
**Figure 3.** Field dependent magnetisation measured in  $\text{NdB}_4$  single crystal for  $H \parallel c$  and  $H \perp c$  using a pulsed magnetic field up to 500 kOe.



**Figure 4.** Temperature dependent resistivity measurements of  $\text{NdB}_4$  made for (a)  $H \parallel c$  and (b)  $H \perp c$ . Each curve is subsequently offset by 2 and 3  $\mu\Omega\text{-cm}$  respectively. Field dependent resistivity measurements made for (c)  $H \parallel c$  and (d)  $H \perp c$ . Each curve is subsequently offset by 2.5  $\mu\Omega\text{-cm}$ . For the panels (a–c) the current,  $I$ , is applied along the  $[110]$  direction, while the current is applied along the  $c$  axis in (d).

The field dependent resistivity measurements for  $H \parallel c$  are shown in Fig. 4(c). As can be seen there are large positive magnetoresistance (defined by  $\text{MR}(H, T) = [\rho(H, T) - \rho(0, T)] / \rho(0, T)$ ) changes at all temperatures, the most significant of which is at  $T = 2$  K with a value of  $\text{MR}(H, T) = 1200\%$  for  $H = 70$  kOe. Large magnetoresistances have also been observed in  $\text{HoB}_4$  with a value of 4000%<sup>20</sup> and in  $\text{GdB}_4$  with a value of 58800%<sup>29</sup>. The resistivity curves at  $T = 2, 3$  and 4 K show features which mirror the plateaux observed in the magnetisation





**Figure 5.** Magnetic phase diagrams of  $\text{NdB}_4$  for (a)  $H \parallel c$  and (b)  $H \perp c$ . For both field directions, Phase I corresponds to a non-collinear antiferromagnetic order, while Phases II and III are two different incommensurate structures. Phases IV and V for  $H \parallel c$  correspond to the  $\frac{1}{5}$ -magnetisation plateau and the fully polarised state respectively.

measurements (see Fig. 2). The most pronounced feature is at 4 K, where there is a decrease in the resistivity at around 28 kOe. A plateau is also observed at  $T = 6$  K, the constant resistivity most likely arising as the system is undergoing a transition from the intermediate to the high temperature phase. This response has also been observed in  $\text{ErB}_4$  and  $\text{TmB}_4$ <sup>30</sup>, where the curves can be thought of as the sum of a conventional orbital magnetoresistance with additional scattering due to magnetic ordering in the plateau state.

The field dependent resistivity curves for  $H \perp c$  are shown in Fig. 4(d). As can be seen there are no noticeable features at any temperature, consistent with the magnetisation measurements. Similarly to the  $H \parallel c$  case, there is a magnetoresistance, which gradually increases with decreasing temperature. The most significant magnetoresistance is again at  $T = 2$  K with a value of  $\text{MR}(H, T) = 2140\%$  for  $H = 70$  kOe.

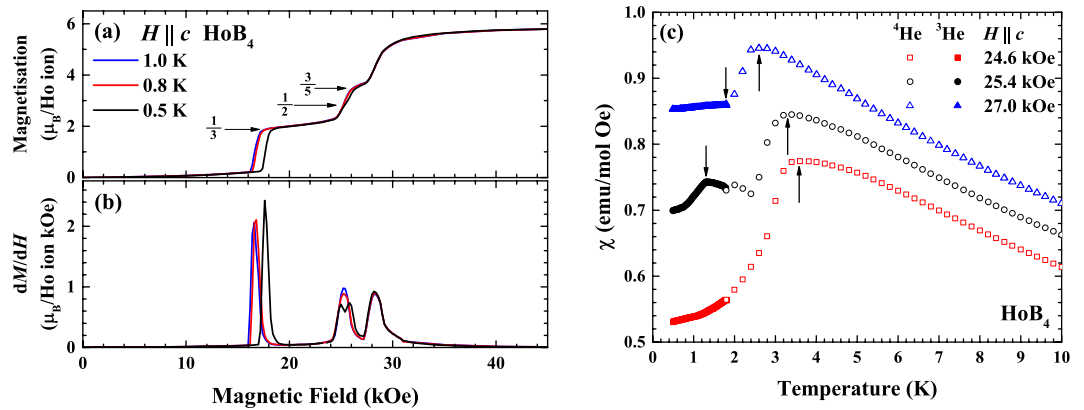
Figure 5 shows the magnetic phase diagrams of  $\text{NdB}_4$  constructed from magnetisation, heat capacity and resistivity measurements for  $H \parallel c$  and  $H \perp c$ . Heat capacity measurements are not shown but are in agreement with previous published results<sup>24</sup>.

For  $H \parallel c$ , Fig. 5(a) the magnetic phase diagram contains five distinct magnetically ordered phases (labelled with Roman numerals I to V) as well as a paramagnetic (PM) phase. The high-temperature Phase I remains largely unaffected by application of a magnetic field. The magnetisation curves suggest no sign of saturation up to 100 kOe. The incommensurate intermediate temperature phase (Phase II) seems to disappear in fields above 30 kOe. The low-temperature zero-field state (Phase III) transforms to Phases IV and V in an applied field with the unusually shaped magnetic transition line between phases III and IV showing a clear minimum at approximately 2 K. Phase V corresponds to the fully polarised phase.

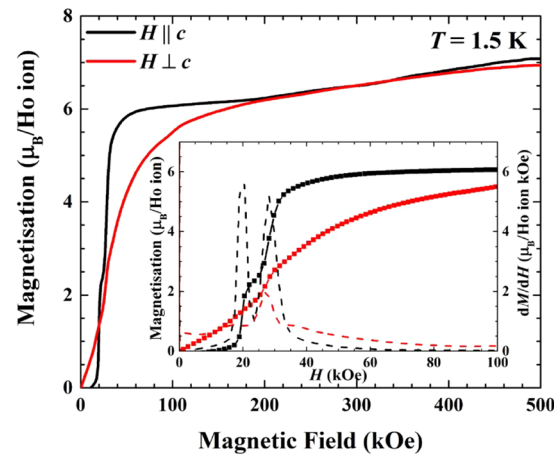
For  $H \perp c$ , the phase diagram (Fig. 5(b)) contains three distinct ordered states (labelled with Roman numerals I to III) as well as the PM phase. Apart from a slight reduction of the transition temperatures (particularly for the PM to the phase I transition) on application of magnetic field, all three ordered phases remain largely unaffected.

**HoB<sub>4</sub>.** Figure 6(a) shows the field dependent magnetisation of  $\text{HoB}_4$  for 0.5, 0.8 and 1 K. The magnetisation curve at  $T = 1$  K shows a magnetisation plateau at  $M/M_{\text{sat}} = \frac{1}{3}$  and a less pronounced feature at  $M/M_{\text{sat}} \approx \frac{3}{5}$ , which is consistent with previous observations at  $T = 2$  K<sup>20,22</sup>. An additional transition has been observed previously at  $M/M_{\text{sat}} \approx \frac{4}{9}$ <sup>23</sup>, this was found to depend on the exact orientation of the crystal with the field. When the  $c$  axis was slightly tilted from the field, the transition is visible, while when the field is aligned along the  $c$  axis it is no longer visible. With temperature decreasing to 0.5 K, the feature at  $M/M_{\text{sat}} \approx \frac{3}{5}$  becomes more pronounced while the transition from zero-field structure to the plateau shifts to higher applied fields. The magnetisation curve at  $T = 0.5$  K shows clear magnetisation plateaux at  $M/M_{\text{sat}} = \frac{1}{3}$  and  $\frac{3}{5}$ , while there is an additional transition occurring at  $M/M_{\text{sat}} \approx \frac{1}{2}$ . This extra feature is highlighted in the differentiated magnetisation curves,  $dM/dH$ , shown in Fig. 6(b), where the  $M/M_{\text{sat}} = \frac{1}{2}$  state is seen as the splitting of the higher-temperature peak of the derivative into two close and partially overlapping peaks around 25 kOe at  $T = 0.5$  K. Interestingly, neutron diffraction measurements<sup>23</sup> revealed that the  $\frac{1}{3}$ -magnetisation plateau is associated with an up-up-down ferrimagnetic stacking along the  $c$  axis. Therefore a two-dimensional SSL model is not well suited for describing the  $M/M_{\text{sat}} = \frac{1}{3}$  plateau. It is, however, possible that the SSL physics is applicable to this new  $\frac{1}{2}$  magnetisation feature.

To investigate this new field-induced state, the temperature dependent magnetic susceptibility measurements were made in a magnetic field of 25.4 kOe corresponding to the local minimum between the two magnetisation jumps in the  $dM/dH$  for  $T = 0.5$  K, as well as in fields just above and below it (see Fig. 6(c)). All three susceptibility curves show a broad maximum at around 3.7 K, which is slightly shifted to lower temperatures by an increasing



**Figure 6.** (a) Field dependent magnetisation and (b) its derivative  $dM/dH$  of  $\text{HoB}_4$  for temperatures below 1 K. The derivative curves highlight field-induced transitions. The magnetisation curves were recorded for both increasing and decreasing fields, but, for clarity, only those corresponding to the increasing field are shown. (c) Temperature dependent magnetic susceptibility at  $H = 24.6, 25.4$  and  $27.0$  kOe. Each curve is subsequently offset by  $0.05 \text{ emu/mol Oe}$ . The arrows correspond to the position of the magnetic phase transitions.



**Figure 7.** Field dependent magnetisation measurements of  $\text{HoB}_4$  for  $H \parallel c$  and  $H \perp c$  using a pulsed magnetic field up to 500 kOe. Inset highlights the fractional magnetisation plateaux at low magnetic fields by showing the magnetisation (symbols) and its derivative  $dM/dH$  (dashed lines).

magnetic field. At  $H = 25.4 \text{ kOe}$ , a clear extra feature is observed in  $\chi(T)$  at  $T \approx 1 \text{ K}$ , which is not seen at either  $H = 24.6 \text{ kOe}$  or  $H = 27.0 \text{ kOe}$ . This observation provides additional support to the claim that  $M/M_{\text{sat}} = \frac{1}{2}$  might be stabilised in  $\text{HoB}_4$  in a narrow field interval at a sufficiently low temperature.

Figure 7 shows the field dependent magnetisation of  $\text{HoB}_4$  in fields up to 500 kOe for both  $H \parallel c$  and  $H \perp c$ . The inset shows the magnetisation curves and derivative in a smaller field range to highlight the transitions observed, which are in agreement with previous measurements<sup>20</sup>. As can be seen the magnetisation initially levels off at  $6 \mu_B$  per Ho ion in a field of approximately 40 kOe and then gradually increases up to approximately  $7 \mu_B$  per Ho ion. For  $H \perp c$ , the behaviour is very different in lower fields, but above 200 kOe the magnetisation curves for  $H \parallel c$  and  $H \perp c$  are practically indistinguishable. During the experiment we have found that upon application of the magnetic field the sample experienced significant torque and had a tendency to deviate away from the  $H \parallel c$  and  $H \perp c$  geometries unless firmly attached to a sample holder. These observations suggest that the  $c$  axis may not be the easy magnetisation direction in  $\text{HoB}_4$  in higher applied fields.

## Summary

We have made detailed investigation of the magnetisation process in  $\text{NdB}_4$  and  $\text{HoB}_4$  single crystal samples at low temperatures.

For  $H \parallel c$ , the dominant feature in magnetisation of  $\text{NdB}_4$  is the  $\frac{1}{5}$ -magnetisation plateau. Our measurements have revealed rather unusual non-monotonic behaviour of critical fields in  $\text{NdB}_4$  where in an applied field of around 15 kOe low temperatures see the field induced magnetic phase be replaced by the zero field structure. For  $H \perp c$ , high field scans have revealed a broad transition at around 70 kOe and a clear slope change in magnetisa-

tion at 150 kOe. Resistivity measurements mirror the transitions observed in magnetisation and heat capacity, they also lead to the observation of a large magnetoresistance for various field directions. Large anisotropy of the magnetic properties of NdB<sub>4</sub> is emphasised by the different shape of the reconstructed  $H - T$  magnetic phase diagrams for  $H \parallel c$  and  $H \perp c$ .

Magnetisation measurements on HoB<sub>4</sub> have revealed the stabilisation of a  $\frac{1}{2}$  plateau, which arises below  $T \approx 1$  K for a narrow field range in addition to the  $\frac{1}{3}$  and  $\frac{3}{5}$  plateaux also seen at higher temperatures. The  $\frac{1}{3}$ -magnetisation plateau in HoB<sub>4</sub> cannot be described within the SSL model<sup>23</sup>, however, the applicability of SSL model to the  $\frac{1}{2}$  plateau is still to be tested. It would be interesting to extend in-field neutron diffraction measurements to sufficiently low temperatures to thoroughly investigate the nature of this new phase. Other RB<sub>4</sub> members, such as ErB<sub>4</sub> and TmB<sub>4</sub><sup>11,30</sup> show a more defined  $\frac{1}{2}$  fractional magnetisation plateau and are well described by the SSL, with the proposed structures centring around antiferromagnetic and ferromagnetic stripes.

The high field measurements on HoB<sub>4</sub> show no further transitions, where the magnetisation curve initially levels off, before there is a slight upturn at 190 kOe that matches the curve where  $H \perp c$ . Both curves gradually increase, reaching  $7 \mu_B/\text{Ho ion}$  at 500 kOe.

## Methods

Polycrystalline rods of HoB<sub>4</sub> and NdB<sub>4</sub> were prepared by arc melting the constituent elements in an argon atmosphere and the floating zone technique using an image furnace with four Xenon-arc lamps was then utilised to grow single crystals. The crystals were checked and aligned using a backscattering x-ray Laue system.

A Quantum Design SQUID magnetometer was used to measure magnetic susceptibility and magnetisation along each of the principal axes between  $1.8 < T < 300$  K and  $0 < H < 70$  kOe. The temperature range was extended to 0.5 K using an iQuantum <sup>3</sup>He low temperature insert<sup>31</sup>. Additional field scans up to 100 kOe were made using an Oxford Instruments vibrating sample magnetometer (VSM) down to temperatures of 1.45 K. High field magnetisation measurements were made using a pulsed magnetic field up to 580 kOe at the Dresden High Magnetic Field Laboratory (HLD), Germany. The measurements were carried out on small (typically less than 10 mg) plate-like samples aligned along a principal axis, such that the field was parallel to the plate face to minimise the demagnetising factor. The demagnetising factor did not exceed a value of 0.22 and therefore the correction for the effective field did not exceed 1% at the transition fields. The demagnetisation factor was determined by following the process outlined by Aharoni<sup>32</sup>. This geometry was used for both  $H \parallel c$  and  $H \perp c$ . AC resistivity measurements were made using the 4-probe method between 1.8 and 300 K in magnetic fields up to 70 kOe using a Quantum Design Physical Property Measurement System. For all resistivity measurements a current,  $I$ , of 10 mA and a frequency of 113 Hz was used with the current applied perpendicular to the field direction.

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## Acknowledgements

The authors are pleased to acknowledge the support of HLD at HZDR, member of the European Magnetic Field Laboratory (EMFL) as well as financial support from the EPSRC, UK, through Grant EP/M028771/1.

## Author Contributions

D.B. grew single crystal with G.B. performed characterisation with M.R.L. analysed the data and prepared the figures and manuscript under the supervising of O.A.P. D.A.M., D.G. and O.A.P. performed the high field magnetisation measurements. N.Q. has offered invaluable discussion and assistance on understanding the system. All authors have reviewed the manuscript.

## Additional Information

**Competing Interests:** The authors declare that they have no competing interests.

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